PATENT SPECIFICATION

(11) 1 275 280

NO DRAWINGS

1 275 280

(21) Application No. 38512/69 (22) Filed 31 July 1969
(31) Convention Application No. P 17 92 185.6
(32) Filed 1 Aug. 1968 in
(33) Germany (DT)
(45) Complete Specification published 24 May 1972
(51) International Classification C01B 25/32
(52) Index at acceptance
C1A D37 G47 G47D37

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(54) METHOD OF PREPARING MINERAL ANIMAL FEED SUPPLEMENTS IN THE FORM OF CALCIUM PHOSPHATE

(71) We, CHEMISCHE FABRIK KALK G.m.b.H., a body corporate organised and existing under the laws of Germany of 22 Kalker Hauptstrasse, Cologne-Kalk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns the preparation of readily absorbed mineral animal feed supplements, comprising calcium phosphates virtually free from fluorine and with a CaO: P_2O_5 molar ratio of from 1 to 2. The calcium phosphate should be in the form of freely running grains, as these tolerate storage well and mix well with other constituents of the feed.

The preparation of pure monocalcium phosphate with a CaO: P_2O_5 molar ratio of 1, for example, for baking purposes, is known from U.S. Patent Specification No. 2,062,064. The method comprises reacting pure calcium oxide or hydroxide with 45—55 Bé gravity strength phosphoric acid in a mixer; this produces a moist, lumpy material with a strong tendency to conglomeration. The material is, therefore, broken up in a disintegrator and then graded, the coarse particles being returned to the disintegrator and the finer ones, of the desired grain size, being dried.

By this method therefore, a free running product can only be prepared in several expensive operations. Another method of making monocalcium phosphate, also consisting of more than one operation, is described in U.S. Patent Specification No. 2,053,266. Calcium carbonate is used as the starting material, which causes a great deal of foam to form during the reaction with the phosphoric acid. Although the phosphoric acid contains approximately 60% by weight P_2O_5, the product obtained in a fast mixer during the first stage of the reaction is still fluid, and can only be converted into small solid particles in a second, slow mixer.

According to U.S. Patent Specification No. 2,296,495, the preparation of monocalcium phosphate can indeed be simplified, by converting dicalcium phosphate and phosphoric acid directly into a granulated product which can be ground, but the starting materials for this method have to be specially prepared. Thus the dicalcium phosphate has to be anhydrous and compact and must be obtained from dicalcium phosphate dihydrate by in one procedure treating it with water and 1% phosphoric acid at temperatures of from 85°C to 96°C. The phosphoric acid must have a P_2O_5 concentration of from 75 to 90% by weight. The reaction has to take place at from 130 to 135°C in order to form pure, anhydrous monocalcium phosphate. Thus additional energy is required, both for concentrating the phosphoric acid and for the reaction itself. Although the method itself is apparently easy to carry out and immediately yields a crumbly product which can be ground, it suffers from the serious drawback that the dicalcium phosphate first has to undergo expensive preparation, if the monocalcium phosphate is to be obtained in the required granular form.

A method of preparing granulated monocalcium phosphate is described in French Specification No. 661,291, although it is only used for making fertilisers containing water-soluble P_2O_5. As the starting materials contain considerable quantities of fluorine, such as would be harmful in animal nutrition and, therefore, could not be used for animal feedstuffs, the Specification did not contain any hint of how to solve the problem of producing mineral feed supplements. Furthermore, the method had serious technical disadvantages, as it is only after several hours' reaction between the starting materials, dicalcium phosphate and phosphoric acid, that a more or less solid or pasty material is obtained, which still has to be dried and granulated.

The problem underlying the invention was how to prepare calcium phosphate suitable for use as a mineral feed additive, with a calcium oxide:P_2O_5 molar ratio of from 1 to 2, while avoiding the above-mentioned drawbacks of known methods, and how to obtain a free-running granulated product in the fewest possible operations.

According to the invention, there is provided a method of preparing granulated, free-running calcium phosphates, for use as mineral animal feed supplements, with a $CaO:P_2O_5$ molar ratio between those of mono and dicalcium phosphate by reacting calcium oxide, calcium hydroxide, dicalcium phosphate without any water of crystallisation or dicalcium phosphate dihydrate with a phosphoric acid containing 45 to 60% by weight of P_2O_5, less than 0.15% by weight of fluorine and less than 10 ppm of arsenic at an elevated temperature, and maturing or drying the final product, wherein a moving bed of the calcium compound is sprayed and reacted with phosphoric acid having a P_2O_5 concentration of 45 to 60% by weight; a $CaO:P_2O_5$ molar ratio of from 1.15:1 to 1.5:1 and a temperature of 30 to 150°C are maintained in the reaction mixture; and the resultant granules are then matured at 15 to 30°C or dried at 80 to 150°C. In this Specification maturation means allowing water present to become water of crystallisation.

The method of the invention uses purified phosphoric acid containing 45 to 60 and preferably 50 to 55% by weight of P_2O_5, less than 0.15% by weight of fluorine and less than 10 parts per million of arsenic. The acid can be obtained by known processes by thermal decomposition of crude phosphate, although it is preferable to use phosphoric acid obtained by converting crude phosphate with mineral acids, separating the corresponding calcium salt, fluorine, lead and arsenic and concentrating the remaining acid. The calcium compounds used according to the invention are calcium oxide, calcium hydroxide, anhydrous dicalcium phosphate or dicalcium phosphate dihydrate of the usual industrial grade. It is preferred that the phosphates produced should not be allowed to contain more than 0.20% fluorine and 15 parts per million arsenic.

In a preferred method of the invention, the calcium compound with a particle size of up to approximately 1 mm, is fed continuously into a mixer, for example of the double roller, granulating drum, granulating plate or fluidised bed type, and kept constantly in motion. The phosphoric acid is sprayed into the moving bed of the calcium compound in the finest possible particles and in quantities such as to keep the $CaO:P_2O_5$ molar ratio between 1.15:1 and 1.5:1 and preferably at 1.2:1. Where a drum is used, the acid is sprayed in through one or more nozzles. In the case of a plate mixer, one nozzle is sufficient, through which the phosphoric acid is sprayed onto the material from above, while in a fluidised bed mixer the acid is introduced from above, preferably through a plurality of nozzles.

The calcium phosphate immediately takes the form of free-running granules, and the time which it has to spend in the mixer depends on the type of apparatus used. In a plate mixer, for example, it would take only a few minutes, whereas it would take the material about a quarter of an hour to two hours to pass through a drum depending on the size of the latter. The reactants are placed in the mixer at room temperature and heated therein, by the heat generated by the reaction, to temperature of from 30 to 70°C, according to the time spent in the machine. The process is carried out at temperatures of from 30 to 150°C. If the heat generated by the reaction is not sufficient to maintain the desired temperature, the phosphoric acid can additionally be warmed by indirect heating. This applies particularly if temperatures of from 110 to 150°C have to be maintained in order to form calcium phosphates free from any water of crystallisation. When the reaction mixture is at temperatures from 30 to 70°C, the calcium phosphates formed do contain such water.

Whichever of the specified starting materials, mixers and temperatures are used, a uniform product, consisting of free-running granules, is obtained directly by keeping the calcium compound in constant movement and spraying it with phosphoric acid in a $CaO:P_2O_5$ molar ratio of from 1.5:1 to 1.15:1 and preferably 1.2:1. The granules are continuously discharged from the mixer and allowed to mature for sufficient time for the water present to become water of crystallisation, or else dried at temperatures of from 80 to 150°C, preferably 120°C. The water content is virtually unchanged by the maturing process, so it is possible to produce a calcium phosphate containing water of crystallisation, whereas if the phosphate is dried at 110 to 150°C, it is virtually free from any water of crystallisation.

The calcium phosphate obtained contains CaO and P_2O_5 in a molar ratio of from 1.5:1 to 1.15:1. The composition of the resultant product is, therefore, between mono and dicalcium phosphate. As a mineral feed supplement, the preferred product has been found to have excellent properties. Owing to its slightly acid taste, it is willingly eaten by cattle, and is readily absorbed. As it is in granular form it is very convenient to store, and even where the relative humidity is high, the product only absorbs a small amount of water. The granular form of the material makes it easier to blend it,

together with other constituents, such as sodium and magnesium compounds, into the usual mineral feed mixes.

The method of the invention will now be further explained with the aid of some examples (the percentages given are by weight).

EXAMPLE 1

800 kg/hr of dicalcium phosphate containing 50% P_2O_5, 28.33% calcium, 0.07% fluorine and 5 ppm arsenic and with a mean grain size of 30μ, is fed continuously into a constantly rotating granulating plate mixer of 1 m diameter, and sprayed continuously through a jet with a 508 kg/hr phosphoric acid containing 52.2% P_2O_5, 0.08% fluorine and 7 ppm arsenic.

A crumbly reaction mixture forms immediately; the mixture stays on the rotary plate for a mean time of 1 minute and reaches a temperature of 30°C. The resultant free-running granulate is discharged continuously and dried at 135°C. Material of over 2 mm is screened off, and the oversize grains are broken up and returned to the screen.

1,210 kg/hr of the calcium phosphate feed supplement is obtained, containing 55% P_2O_5 of which 75% is water soluble, the $CaO:P_2O_5$ molar ratio being 1.2:1. The various grain sizes are in the following proportions:

1 to 2	mm	...	45%
0.5 to 1	mm	...	27%
0.2 to 0.5	mm	...	24%
0.2	mm	...	4%

The storage properties of the granules were tested for four months in presses 0.4 m in diameter and 0.5 m in height, at a pressure of 1.45 kg/cm². The walls of the presses contained holes, giving the air free access to the granules. The granules remained free-running for the whole period of the test.

EXAMPLE 2

2,400 parts by weight of dicalcium phosphate, containing 50% P_2O_5, 28.33% Ca, 0.07% F, 5 ppm As and with a mean grain size of 30μ, is fed into a double roller mixer and kept constantly moving. Shortly after the place where it is fed into the mixer, the dicalcium phosphate is sprayed through a nozzle with 1,667 parts by weight of phosphoric acid, containing 48% P_2O_5, 0.07% F and 6 ppm As. A crumbly reaction mixture forms immediately, is kept in the mixer for 5 minutes and reaches a temperature of 50°C. The resultant free-running granulate is allowed to mature for 4 hours at 20°C.

The yield is 4000 parts by weight of calcium phosphate feed supplement, containing 50% P_2O_5 of which 75% is water soluble, the $CaO:P_2O_5$ molar ratio being 1.2:1. Immediately after maturing, the grains range in size from 0.06 to 5.0 mm. They are then ground in a mill to give grain sizes in the following proportions:

1 to 2	mm	...	32%
0.5 to 1	mm	...	36%
0.2 to 0.5	mm	...	24%
0.2	mm	...	8%

EXAMPLE 3

707 parts by weight ground calcium oxide (95%) are sprayed with 2,731 parts by weight of phosphoric acid containing 52% P_2O_5, 0.08% F and 7 ppm As, in a rotary drum mixer. A crumbly reaction mixture forms immediately, is kept in the drum for 20 minutes and reaches a temperature of from 110 to 130°C. The resultant free-running granulate contains 52.3% P_2O_5.

The material is dried further in a rotary tube drier, to give 2,580 parts by weight of the calcium phosphate feed additive, containing 55% P_2O_5 of which 75% is water soluble, the $CaO:P_2O_5$ molar ratio being 1.2:1. After grinding in a mill, the following grain sizes are obtained:

1 to 2	mm	...	43%
0.5 to 1	mm	...	24%
0.2 to 0.5	mm	...	28%
0.2	mm	...	5%

EXAMPLE 4

2,485 parts by weight per hour of dicalcium phosphate, containing 40% P_2O_5, 22.6% Ca, 0.07% F, and 5 ppm As, 819 parts by weight per hour of phosphoric acid, containing 52% P_2O_5, 0.08% F and 7 ppm As, and 8,000 parts by weight per hour of recycled material are fed continuously into a granulating plate mixer. A crumbly reaction mixture forms immediately, is kept on the plate for approximately 1 minute and reaches a temperature of about 40°C. When the material has been finally dried and ground and the appropriate amount recycled, 2,840 parts by weight per hour of the calcium phosphate feed additive are obtained, containing 50% P_2O_5 of which 55% is water-soluble, the $CaO:P_2O_5$ molar ratio being 1.4:1.

The final product contains the following grain sizes:

1 to 2	mm	...	40%
0.5 to 1	mm	...	29%
0.2 to 0.5	mm	...	25%
0.2	mm	...	6%

The suitability of the phosphorus contained in the calcium phosphate produced according to the invention for animal nutrition was tested by the rat test described in the "Zeitschrift für Tierphysiologie, Tierer-

nährung und Futtermittelkunde", Volume 16, (1961) No. 2, Pages 97 to 118. By this method young, growing Albino rats are fed for 14 days on the diet being tested. The test diet consists of a basic feed in which the mineral supplement to be tested is included.

The increase in the weight (Z) of the experimental animals over the whole duration of the test is noted, and their skeletal development is ascertained from X-ray photographs in which the region of the knee-joint (F) is specially measured. A reference value B is calculated, on the basis of series of tests with harmonised feedings:

$$B_{(1-3)} = \frac{Z \times 5.6}{F}$$

B_1 is a rachitis diet, giving the minimum value for Z and the maximum for F, B_2 is a controlled or balanced diet, containing just as much phosphorus as that being tested, and B_3 is the phosphorus containing diet being tested. Thus the phosphorus containing diet to be tested is compared with the rachitis diet and the balanced one. The effectiveness of the diet being tested is then calculated as follows:

$$\text{Effectiveness} = \frac{B_3 \times 100}{B_2 - B_1}$$

An effectiveness of 70 to 90 is satisfactory and from 90 to 110 good.

By this test the calcium phosphates prepared according to the invention have an effectiveness of 106, whereas dicalcium phosphate has an effectiveness of approximately 75.

The phosphates can be applied to animal feedstuffs for example as described in our copending Patent Application No. 36976/69 (Serial No. 1,257,691), to which reference is directed.

WHAT WE CLAIM IS:—

1. A method of preparing granulated, free-running calcium phosphates, for use as mineral animal feed supplements, with a $CaO:P_2O_5$ molar ratio between those of mono and dicalcium phosphate, by reacting calcium oxide, calcium hydroxide, dicalcium phosphate without any water of crystallisation or dicalcium phosphate dihydrate with a phosphoric acid containing 45 to 60% by weight of P_2O_5, less than 0.15% by weight of fluorine and less than 10 ppm of arsenic at an elevated temperature, and maturing or drying the final product, wherein a moving bed of the calcium compound is sprayed and reacted with phosphoric acid having a P_2O_5 concentration of 45 to 60% by weight; a $CaO:P_2O_5$ molar ratio of from 1.15:1 to 1.5:1 and a temperature of 30 to 150°C are maintained in the reaction mixture; and the resultant granules are then matured at 15 to 30°C or dried at 80 to 150°C.

2. A method according to claim 1 wherein the $CaO:P_2O_5$ molar ratio maintained in the reaction mixture is 1.2:1.

3. A method according to claim 1 or 2, wherein the phosphoric acid contains 50 to 55% by weight of P_2O_5.

4. A method according to claim 1, substantially as hereinbefore described in any of the Examples.

5. A phosphate made by the method of any preceding claim.

6. An animal feedstuff including a phosphate according to claim 5 as a mineral supplement.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1972.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.